On the Positive Ionization from Certain Hot Salts, together with some Observations on the Electrical Properties of Molybdenite at High Temperatures.

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On the Positive Ionization from Certain Hot Salts, together with some Observations on the Electrical Properties of Molybdenite at High Temperatures.

A DISSERTATION

PRESENTED TO THE

FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

A. T. WATERMAN.

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On the Positive Ionization from Certain Hot Salts, together with some Observations on the Electrical Properties of Molybdenite at High Temperatures.

By A. T. WATERMAN, *Princeton University* *.

THE general problem as to the character of the ionization from hot bodies has been examined in considerable detail during recent years. The results obtained from experiments with metallic strips indicate, on the whole, no characteristic emission, but one which is apparently the same for all the metals and due no doubt, so far as the positive emission is concerned, to some common impurity. The positive emission is now generally considered to consist mainly of potassium atoms with a single charge ; the negative of electrons.

From experiments with various salts the following general conclusions have been reached, although there are exceptions :—

I. Positive emission : characteristic of the metallic constituent.

II. Negative emission : electrons accompanied in some cases by an emission characteristic of the remaining constituent.

The metals whose salts (chiefly the halides and sulphates) have been investigated are :—

Alkaline group : K, Na, Li, Rb, Cs.
Alkaline-earth group : Be, Mg, Cd, Zn, Sr, Ca, Ba ; and Al, Mn, Fe.

* Communicated by Prof. O. W. Richardson, F.R.S.

Of these the Zn and Cd halides give a positive emission consisting of doubly charged atoms.

Mn and Al vary considerably in their emission, so that nothing very definite can be said about them.

Be and Fe apparently give only the K-impurity emission like that from the pure metals.

All the rest yield a positive emission consisting of singly charged atoms of the metal.

The question naturally arises as to the reason for obtaining a singly charged ion in some cases and a doubly charged in others. This does not appear to be connected simply with the valence as might be expected. In other words, how can one predict what the emission from a given salt will be? The experiments that follow were instituted with a view to attempting an answer to this question. Only positive emission was considered and a number of salts were tried, the metals of which differed in valence.

The following were the salts employed :—

$AgCl$	Cu_2Cl_2
$AgBr$	AlF_3
$PbCl_2$	$PtCl_2$
$PbBr_2$	
$CuCl_2 . 2H_2O$	MoS_2 (mineral form).

Method.

The method employed was identical with that used by Prof. Richardson in his article on "The Ions from Hot Salts," published in the Phil. Mag. for September 1913, pp. 452–472. Briefly, the salt is placed on a narrow strip of platinum whose emission has previously been driven out by continued heating to a temperature above which measurements with the salt are to be made. The salt is then heated by passing a current through the strip, and the temperature roughly ascertained from the resistance of the strip. If now the strip is raised to a certain potential, emission from the hot salt is driven off. A magnetic field is then applied which deflects the stream of ions. The amount of this deflexion is taken when the magnetic field is reversed. This deflexion obviously depends on

1. The dimensions of the apparatus.
2. The potential applied.
3. The strength of the magnetic field.
4. The value of e/m for the ions.

The formula connecting these quantities is :

$$\frac{e}{m} = \frac{9}{2}\frac{\mathrm{V}x^2}{\mathrm{H}^2 d^4}, \quad \ldots \ldots \ldots \quad (1)$$

where V = potential, H = strength of field, d = distance between strip and plate which receives ions, and x = half the deflexion caused by reversal of field.

All these quantities were measured as described in Prof. Richardson's article on "Positive Ions from Hot Metals" †.

The platinum strip was cut with narrow and short constrictions, one on each side of the centre. When a current was passed through, these constrictions would become hotter than the rest of the strip, and thus would tend to hold in place a salt lying between them.

The accuracy of the results of the experiment was found to depend upon the accuracy with which the distance d could be measured and kept constant. To accomplish this end two methods of mounting the strip were used :—

(*a*) A very short strip was made ; its ends were soldered to two heavy brass strips connected to the lead wires for the heating circuit. It was thought that the shortness of the strip would diminish the bending due to changes in temperature and hence length. This method was found to be not altogether satisfactory.

(*b*) A longer strip was used, fastened at one end rigidly to the end of one lead wire, and at the other to a phosphor-bronze spring acting as the other lead wire. This spring was under tension sufficient to take up any increase in length and to hold the strip level. When carefully adjusted this mounting was very successful.

The making and successful mounting of a perfect strip is rather a delicate operation. This, together with the inevitable subsequent variations in the distance d and many other difficulties, made an exact experiment a tedious process.

The temperature-resistance curve of a test Pt strip in air was drawn by taking the following as fiducial points :—

Room temperature.
Boiling water.
Melting point of $NaNO_3$.
" " " Borax.
" " " Na_2SO_4.

* Richardson, Phil. Mag., Nov. 1908, p. 740.
† Roy. Soc. Proc. A. vol. lxxxix. p. 507 (1914).

The graph was a perfect straight line as nearly as could be seen. Knowing the resistance at room temperature of the strip actually used in the experiment, the same fiducial points could be calculated for it and a similar temperature-resistance curve obtained. From these the temperature of the strip could be inferred from its resistance with a fair degree of approximation. The actual resistance of the strips used when cold varied from ·3 to ·8 ohm.

The method of measurement was chiefly the "balance" method as defined by Richardson *, but readings by the "slit" method were taken whenever feasible.

The pressure in the tube in which the strip and connexions were enclosed was always less than 10^{-4} mm. of mercury.

In the tables that follow, m/H is the ratio of the mass of the ion to that of an H-ion in electrolysis on the supposition that it carries an equal charge. The charge of an H-ion was taken to be 9649 electromagnetic units. B and S refer to the "balance" and "slit" methods of measurement respectively.

1. *Silver Chloride.*

(*a*) The first specimen used was probably fairly pure, but it was considerably darkened by exposure. A very small amount was moistened with distilled water and placed on the strip, mounted by method (*a*). The emission from the strip had been driven out for all temperatures below 1000° C. Above this point considerable emission from the Pt would certainly be present.

The melting point of AgCl is given as 450° C. Permanent emission was first detected at about 400°, but was at that point too small to admit of measurement.

V.	H.	Method.	Temperature.	Mean values. e/m.	m/H.
160	1487	B & S	460° to 1100°	254·4	37·9

The values for e/m were quite consistent—within about 3 per cent. variation from mean—and some forty readings were taken.

(*b*) Another specimen of the same salt was placed on the strip under the same conditions, giving the following results :—

V.	H.	M.	T.	e/m.	m/H.
140	2030	B & S	465° to 940°	259·8	37·1

* Phil. Mag., Sept. 1913, p. 453.

This value for e/m is the mean of thirty readings in even better agreement than in the previous case.

(*c*) An attempt was made to see whether freshly prepared AgCl would yield the same results. This specimen was prepared from the purest $AgNO_3$ and HCl obtainable, and kept as far as possible from the light. The salt was precipitated in the form of heavy white flakes, and the greatest difficulty was found in keeping the salt on the strip when it was heated.

A fresh strip of Pt was inserted and measurements were taken on its emission to check the accuracy of the later experiments with AgCl. It was glowed until no appreciable emission was detected below 1250° C. It was mounted by method (*b*).

V.	H.	M.	T.	e/m.	m/H.
203	2460	B & S	1000° to 1120°	247·5	38·9 dry salt.
203	2460	B	790° to 1130°	244·6	39·4 moistened with distilled H_2O.

These values were the mean of a number of readings as consistent as the former.

(*d*) Silver Iodide. This salt was furnished by Eimer & Amend with no specifications as to its purity. A Pt strip, mounting (*b*), was used on which $PtCl_2$ had previously been tested, but which had been glowed for points below 1200° C.

The melting point of AgI is given as 527° C. The initial emission was looked for with extreme care, and the first signs of it appeared at 520°. It was far too small to measure, and died away very quickly. A definite emission was found at 575°.

V.	H.	M.	T.	e/m.	m/H.
204	2460	B & S	650° to 1195°	267·3	36·2

These values, about twenty in number, of which these are the mean, were also very consistent although slightly lower than the preceding for AgCl. The difference is probably due to the distance d varying.

Conclusion.—The values here given for m/H for AgCl and AgI do not point to any characteristic silver emission which can be detected, the atomic weight of Ag being 107·88. The numbers were quite consistent and averaged a little lower than the K impurity emission from metals, for which $m/H = 39$.

Furthermore, the readings could only be taken at temperatures for which at such low pressures the salt must have been vaporized. If an impurity were present of low volatility, *e. g.* the common salts of potassium, it would remain on the strip and become active.

In cases (*a*) and (*b*) considerable metallic silver was known to be present. In (*c*) the distilled water alone would be enough to account for an emission at 800° and over (see § 6).

2. *Cuprous Chloride.*

(*a*) The first specimen was made by Kahlbaum, but the salt had been exposed to the air for a long time, so that it was light green in colour, due no doubt to partial oxidation to $CuCl_2$. The salt was deposited dry on a Pt strip, of mounting (*a*), which had been glowed up to 1000° C. The melting point of Cu_2Cl_2 is given as 434° C.

V.	H.	T.	M.	*e*/*m*.	*m*/H.
156 & 168	1487	533° to 1100°	B	358·0 to 311·6	27·0 to 31·0
156	1487	530°	S	413·0	23·35
				392·8	24·55
				392·0	24·6
				405·0	23·8
168	1487	1000°	S	376·8	25·6
	From a single curve			387·4	24·9
				311·6	31·0

The values of *m*/H by the balance method rose steadily from around 27 at 530° to about 31 at 1000° and remained there. The only distinct values obtained by the slit method are given above. They appear to be due to Na impurity —*m*/H = 23—at the lower temperature. At the higher the Na^+ value still continues with one reading of a possible Cu^{++} ion. There is evidently more than one kind of ion involved.

(*b*) A pure sample of Cu_2Cl_2 was used for this experiment, —Kahlbaum's "zur Analyse." It was placed on a Pt strip, mounted by method (*b*), which was used for experiments with $PtCl_2$ and AgI, but which had been glowed for points below 1100° C. The salt was white and semi-transparent.

V.	H.	M.	T.	*e*/*m*.	*m*/H.
205	2460	B & S	870° to 1200°	280	34·4

About twenty readings were taken, which ran from about 35 at 900° to 32·5 at 1100°. The few readings taken by the slit method gave values around 32·5, except one at 900°, the only one taken below 1100°, which gave 35·9.

Conclusion.—From these values of m/H it certainly would seem as if a Cu^{++} ion had been detected. The first specimen (*a*) evidently was not at all pure, but there were signs of a doubly charged ion at high temperatures. When emission first set in with (*b*) the values were uncertain. At the higher temperatures there are still more positive evidences of a Cu^{++} ion, for which $m/H = 31·6$.

In any case there is probably no emission of Cu-ions under 1000° or so. At this temperature and pressure, however, the salt must long since have been vaporized. If there is an emission of Cu-ions then, it seems likely that it must come from the action of the Pt on the vapour. This was shown to be possible by Sheard *.

Cupric Chloride : $CuCl_2$, $2H_2O$.

(*c*) This salt was probably very pure—Kahlbaum, kryst, "zur Analyse." Its melting point is 498° C. At 100° $CuCl_2$ with water of crystallization loses half its chlorine to form Cu_2Cl_2. This action was confirmed.

The Pt strip, mounting (*b*), on which measurement was made had been glowed below 1100°. Emission from the salt was first detected at 780°. A great deal of trouble was experienced in keeping it on the strip when dry.

V.	H.	M.	T.	*e/m.*	*m*/H.
204	2460	B & S	840° to 1200°	266·3	36·3 dry crystals.
204	2460	B	870° to 1050°	266·3	36·3 „ „

Conclusion.—This does not seem to be anything more than the regular impurity emission. The value is, however, a little low. As $CuCl_2$ is supposed to go over into Cu_2Cl_2 at 500°, this may be taken as evidence that the emission from Cu_2Cl_2 in (*a*) and (*b*) above is not characteristic Cu emission, but a combination of K and Na impurities for instance. Nevertheless, it is difficult to ascribe the very distinct values about 32 to an increase in the distance *d*. 32 as a low value for 39 is perhaps possible but not probable. It may thus be that the value 36·3 in (*c*) was due to a mixture of Cu^{++} and K^+ ions. In that case a characteristic Cu^{++} emission would take place in both cases. At all events there certainly is no sign of a singly charged ion of Cu.

* Phil. Mag., March 1913, p. 370.

3. *Lead Chloride.*

(*a*) The salt used for this test was primarily very pure, but it had undergone considerable exposure to the air. Its melting point is 500°.

The salt was moistened with distilled water and placed on the same strip, mounting (*a*), on which Cu_2Cl_2 and AgCl had been heated. The strip gave no significant emission below 1000°.

Emission was first detected at 460°, but it was too small for measurement and almost immediately died away. No emission was then found until 600°. This steadily increased with rise in temperature and readings were taken at 820°. The increase of emission with temperature was much less than with any of the other salts.

In making observations with the slit method when the emission was fairly large, curves were found with more than one maximum. In this case it seemed probable that this arose from different parts of the salt emitting rather than from there being more than one kind of ion present in any quantity. This was concluded partly from the shape of the curves; partly from the fact that the balance method gave results that were fairly steady; and from the fact that the values of m/H, calculated for a possible two kinds of ions (there being two distinct maxima), seem very unlikely. For instance, in a typical curve, the ions would have to be

$$m/H = 18{\cdot}6 \quad \text{and} \quad m/H = 357{\cdot}5$$

on this supposition.

The mean values for twenty readings follow:—

V.	H.	M.	T.	*e*/*m*.	*m*/H.
170			820°		
203	2030	B & S	to	259·9	37·0
			940°		

The balance method gave results varying from 35·5 at first to 39 at higher temperatures. The slit method, if interpreted as above, gave about 39.

Lead Bromide.

(*a*) This salt was of about the same purity as the $PbCl_2$ just described. Its melting point is 400°. It was moistened with distilled water and placed on the strip just used for $PbCl_2$. The emission from the strip was negligible below 925°.

First signs of emission from the salt occurred at 400°, but soon died out. A fairly permanent emission appeared at 470°. The following mean values were obtained :—

V.	H.	M.	T.	*e/m.*	*m*/H.
112	2030	B & S	530° to 1130°	264·3	36·5
202	2030	B & S	460° to 490°	254·4 fresh salt	37·9

The balance and slit methods were in good agreement.

(*b*) The same $PbBr_2$ was used for this determination. A different Pt strip was employed on which AlF_3 had been heated. The emission from the strip was not comparable with that from the salt up to 1150°. The salt was put on with distilled water and the emission watched for very carefully.

Emission so very slight as almost to escape attention started at 100°, reaching a maximum at 400°, and then dropping to zero. Permanent definite emission set in at 560° and reached a measurable value at 660°. The strip was mounted by method (*b*) and the values were therefore much more consistent, agreeing within 1 per cent. almost all the time :

V.	H.	M.	T.	*e/m.*	*m*/H.
204	2460	B & S	690° to 1075°	278	34·7

Conclusion.—The values of *m*/H for $PbCl_2$ and $PbBr_2$ are fairly consistent. There is no evidence of an emission characteristic of the Pb, for which it might be expected $m/H = 103{\cdot}5$.

The values seem quite evidently to be due to K as an impurity, although at times they are rather low.

It is possible that a characteristic emission of Pb was obtained in the last experiment with $PbBr_2$, namely, the very slight emission detected from 100° to 400°. It was, however, far too slight for measurement.

4. *Aluminium Fluoride.*

Only one experiment was made with this salt, the specimen used being made by Kahlbaum. The melting point of AlF_3 is probably about 150°.

The salt was moistened with distilled water and placed on a new strip from which the emission had been driven out below 900°. The mounting was by method (*b*).

Emission from the salt was first detected at 150°, although here it was barely noticeable and soon passed away. At 620° it admitted of measurement. Some thirty readings were taken, as follows :—

V.	H.	M.	T.	*e*/*m*.	*m*/H.
			660°	175·5	55
204	1000	B	to	to	to
			840°	224·7	43
,,	,,	S	740°	241·2	40·0
				232·6	41·4
,,	,,	,,	815°	225·2	42·8
				212·3	45·4
,,	,,	,,	830°	211·8	45·5
				223·5	43·2

The values by the balance method at first ranged around 55, coming steadily down as the temperature increased to 43.

Conclusion.—The values for Al^{+}, Al^{++}, and Al^{+++} would be $m/H = 27{\cdot}1$, 13·5, and 9, respectively, so that there is apparently no Al emission at the above temperatures. Judging by the very low boiling-point the salt could only be in a state of vapour, and the emission above could be accounted for, in part at least, by the distilled water (see § 6). It is evident that the K emission is present, but whether the high values by the balance method are caused by the presence of some heavy ion or are due to the motion of the strip is a matter of doubt.

It is unfortunate that the initial emission beginning with 150° was too small and transient to measure.

5. *Platinum Chloride.*

(*a*) This salt was made by dissolving some clean strips of platinum in aqua regia. The solution was evaporated to dryness and the residue dissolved in distilled water. The washing process was repeated a number of times. Glass vessels were used throughout. A drop of the solution was finally placed upon the Pt strip, mounting (*b*), which had previously been used for AlF_3 and $PbBr_2$. The strip was glowed for temperatures below 1150°.

Emission was first detected at 550° and was measurable at 600°. It appeared to decay very rapidly, and measurements were first made at 720°.

V.	H.	M.	T.	*e*/*m*.	*m*/H.
204	2460	B	723°	268	36
			to	to	to
			945°	358	27
			to	to	to
			1100°	284	34

The values, some forty in number, decreased steadily with rise in temperature, and slightly with time at constant temperature, from 36 to 27, and then rose with increasing temperature to 34. The values by the slit method did not go lower than 30, but observed the same decrease and later rise.

(*b*) As the $PtCl_2$ used in the above determination was made in a glass vessel, and as glass is known to be quite soluble in aqua regia, a further quantity of $PtCl_2$ was prepared in a platinum crucible, so as to be more completely rid of this impurity. This does not remove it altogether, however, as glass is soluble to a slight degree in the HCl used. About sixty readings were taken :—

V.	H.	M.	T.	*e*/*m*.	*m*/H.
204	2460	B	780° to 945° to 1130°	256·1 to 264·3 to 256·5	37·6 to 36·5 to 37·5
„	„	S	930° to 1100°	256·1	37·6

The values were remarkably consistent and did not show any appreciable decrease until after long heating at 930°.

Conclusion.—No emission was found characteristic of Pt, unless it be taken as significant that $PtCl_2$ and a Pt strip give practically the same value of *m*/H. At any rate there appears to be no connexion with the atomic weight of platinum.

The presence of glass as an impurity would warrant the lowering of *m*/H due to Na compounds contained. That this is the case becomes more plausible when in (*b*) precautions are taken to keep the glass out as far as possible. The same decrease occurs but to a much less degree.

The emission seems to be without doubt due to K as an impurity.

6. *Sources of Impurities.*

As has already been touched upon, it is well known that a Pt strip, in fact apparently any strip of metal, no matter how carefully it is cleaned, gives off a decided positive emission when heated. It is quite persistent and does not appear to be characteristic of the metal, but may most probably be due to potassium in some combination as an impurity.

Now it has been shown * that a Pt strip which had lost

* Horton, Roy. Soc. Proc. A. vol lxxxviii. p. 131 (1912).

its power of emitting would regain it to some extent if heated in air. Several attempts have been made here to determine just how much this source of impurity entered into the ordinary manipulation of the apparatus.

A Pt strip was glowed until it showed no emission whatever below 1000°. The intensity of the emission was taken at 1150°, and the strip was allowed to cool in the vacuum. Dry air was admitted for one minute and immediately pumped out again. A reading of the emission was taken at the same temperature as before. The same thing was done after exposing the strip to cold dry air for 25 hours. Then the strip was removed and placed in a box for 42 days, exposed to the ordinary air in the room, and a reading taken again. The readings are given for the velocity of the electrometer spot in decimetres per second.

Then the same strip was tested in the same manner, being touched between readings with the Pt wire used to place the test salts on the strip. The wire always previously gave a negative flame test.

A further trial was made, placing a drop or two of distilled water on the strip between readings.

The results follow :—

	Time. hrs.	Time. min.	T°. C.	Intensity of emission.	Remarks.
Pt strip alone.	0	0	1150°	·290	
Cold dry air admitted for one minute.					
	0	1	1150°	·320	Decaying
	0	4	„	·303	fast.
	0	6	„	·279	Fairly
	0	8	„	·275	steady.
Air admitted for 25 hours.					
	25	8	1150°	·376	Decaying.
	25	13	„	·351	
	25	18	„	·336	Fairly
	25	28	„	·324	steady.
Exposed to air for 42 days.					
	42 days		805°	·161	

(See measurement (A) of *e/m* here.)

	hrs.	min.	C.	Intensity.	Remarks.
Pt strip	0	0	1050°	·01	Increasing.
alone.	0	5	„	·200	Steady.
Distilled water placed on strip with Pt wire.					
	0	8	725°	·01	
	0	11	870°	·45	
	0	14	930°	2·50	

(See measurement (B) of *e/m* here.)

When touched by a Pt wire between readings the emission at 1150 was increased only 10 per cent., which can be accounted for simply by the exposure to the air in taking out the strip.

The distilled water was made in a block tin vessel and kept in a bottle washed repeatedly with distilled water, but not boiled. It was the same water which was used in laying the various salts on the Pt strip in the previous experiments.

Measurements on m/H from the strip (see above) :

	V.	H.	M.	T.	m/H.	
(A)	203	2460	B	1027°	40·1	Pt strip after long
	„	„	„	1090°	36·7	exposure to air.

Strip glowed out to 1100°.

	V.	H.	M.	T.	m/H.	
(B)	204	2460	B	930°	37·7	Strip plus distilled
	„	„	„	933°	36·7	H_2O.

From these investigations of the sources of impurities in handling the apparatus it appears that the salts which it was possible to mount on the strip dry were practically uncontaminated, as far as the process of mounting went. The only chance for impurity not already in the salt would be a very slight amount from exposure to the air.

As for the salts mounted with water, if no emission below 800° could be obtained sufficient to take readings, the chances are that the emission from the water would figure largely in the results. By emission from the water of course emission from impurities brought in with the water is meant. If emission was obtained at temperatures below 700°, it is likely that the emission due to the water would not enter into the results.

A very noticeable characteristic of these impurities is that they are not at all lasting. The decay was found to be quite rapid for every case except the one where the Pt strip was exposed to the air for 42 days. In this case the emission was found to increase considerably at constant temperature for a short time after heating was begun.

7. *Molybdenite.*

This mineral appeared to be well adapted for measurements with this apparatus. It occurs in the form of flat sheets, rather soft, of a metallic lustre, and very sectile.

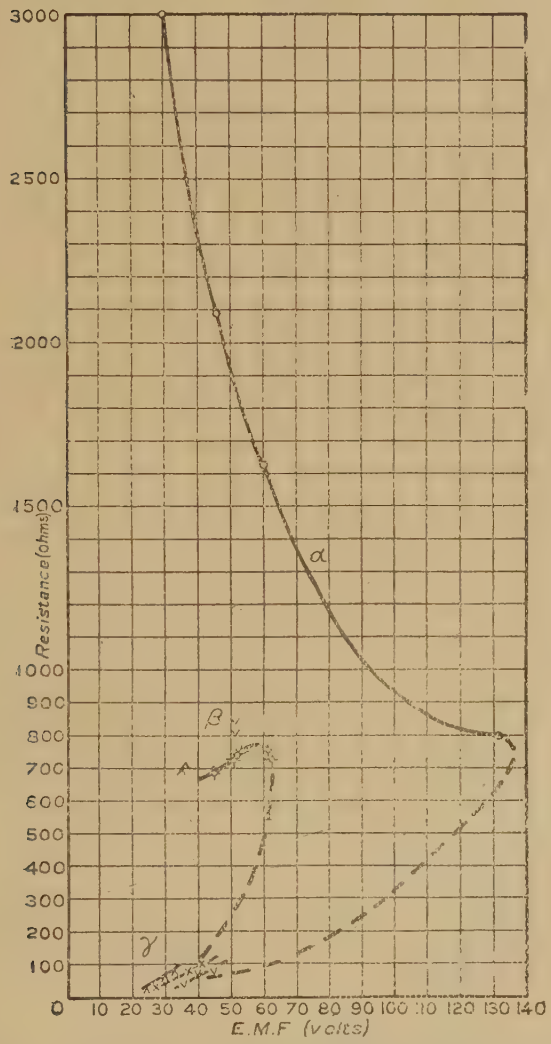
Strips are quite easily prepared for use. But it is not readily soldered. For this reason the method of mounting was changed somewhat, and two small brass screw clamps were employed to hold the ends of the strip. It was difficult to obtain a uniform contact for all variations in temperature, as on account of the softness of the mineral too much pressure could not be applied at the clamps without crushing the strip to a powder, whereas too little pressure meant serious instability of resistance. The surface of the strip was flush with the lower plate of the apparatus for measuring e/m when cool, but no arrangement was used to make certain that it was thus when hot. The thickness of the strips was about 1·5 mm., somewhat greater than that of the Pt strips used, otherwise the dimensions were practically the same.

The electrical conductivity of molybdenite presents peculiar and interesting features. With small applied potential differences the resistance of the strips is very high, but diminishes rapidly with increasing potential differences. No doubt this alteration in conductivity is partly due to the rise in temperature caused by the electric current, and is similar to the effects shown by a large number of minerals which have been examined in detail by Kœnigsberger and Schilling *. The effect does not, however, appear to be entirely, or perhaps even principally, a temperature effect, since it is shown under very low voltages when the currents are too small to cause any perceptible increase in the temperature of the material. Thus with one strip the resistance was $8{\cdot}1 \times 10^5$ ohms for 2 volts applied potential difference and $3{\cdot}52 \times 10^6$ ohms for 0·1 volt. The diminution of resistance with increasing potential difference continues uniformly up to a certain potential difference, which varies to some extent with different specimens and according to the treatment to which they have been subjected; at this point, which will be referred to as "the break," the resistance diminishes suddenly and the mineral conducts, at a red heat, with a comparatively low resistance. Before the voltage has been raised sufficiently for the break to occur the resistance diminishes, as has been noted above, with increasing voltage, whereas after the break the resistance diminishes with diminishing voltage. This difference may be regarded as characteristic of two states, α and β, of the material which occur before and after the break. The phenomenon of the break is reversible, but the rate of change of state decreases after long heating. The substance also tends to persist in the state in which it was when the current was turned off.

* *Ann. der Phys.* vol. xxxii. p. 179 (1910).

For example, when, after passing through the break and turning off the current, gradually increasing potentials were

Fig. 1.



applied, the resistance was found to increase with increasing potentials up to a potential a little below that at which the break occurred. These relations are exemplified in fig. 1.

The portion (α) of the curve represents the initial heating before the break; the group of points (β) was taken after the break; the group (γ) was obtained after the strip had been heated for a long time in the second state. Lines are drawn connecting the definite consecutive readings. The dotted line represents the break or change in state. The portion (α) of the graph for low values of the potential has the form of approaching the vertical axis asymptotically; the value of the resistance for a potential difference of two volts was 40,100 ohms, for instance. Results of the same general character as those indicated were obtained with different strips, and when the resistances and potential differences were measured in a variety of ways.

As the break was approached the values of the resistance for a given potential were observed to decrease with time; so that often a considerable interval elapsed before the resistance reached a steady value. Beyond the break it was often difficult to maintain a steady resistance. The resistance of one of the strips under constant voltage was measured at 24° C., 100° C., 262° C., and 316° C. The break was found to occur at 310° C. Below the break the resistance varied with the absolute temperature T in accordance with the formula $Ae^{b/T}$, where A and b are constants. Normally molybdenum sulphide belongs to the hexagonal class of crystals, type dihexagonal equatorial. In the experiments the heating current was passed through the strips at right angles to the crystallographic "c" axis. There is no evidence of any change of crystalline or chemical structure at the break unless a sudden rise in temperature observed at that point can be so interpreted. The variation of resistance with current for very small currents and the tendency to persist in the second state, already alluded to, suggest that the electrons are liberated in the material, partly by the action of the electric field and not merely as a result of the increase of temperature. Apparently the best condition for a quick return from the second to the first state is the presence of a small current, but one which is not zero. Professor A. Trowbridge has shown that the sign of the Hall effect in molybdenite indicates that the current is carried by negative electrons.

8. *Emission.*

The first experiments to determine e/m, made by the method used in dealing with the salts as described in the

earlier part of this paper, gave very erratic results. It was felt that this might be caused by the drop of potential along the molybdenite strip owing to its high resistance. This makes the value of V to be substituted in the formula for e/m uncertain even when, as in most of the experiments, the potential is applied at the middle of the strip by means of a sliding contact to an external high resistance shunt. Even in this case the correct effective potential will only be that at the centre of the strip provided the emission is symmetrical about the centre. This difficulty might have been overcome by measuring the magnetic deflexions with the heating currents successively in opposite directions, but this method was not found to be practicable. The methods finally adopted were (1) heating the molybdenite strip directly by an alternating current, and (2) heating the molybdenite on an auxiliary strip of platinum.

On searching for a positive emission from the strip a very slight amount was observed in all cases when the strip was now at a point considerably below the break. This was transient and could not be measured. Permanent emission commenced just below or just at the start of the break, and it is here that measurements were commenced. The substance at red heat is very active in its emission, so that as the temperature was increased the sensitiveness of the electrometer had to be decreased by adding capacities to the pair of quadrants in order to get anything like accurate readings. Except in a few instances the balance method was the only one by which good results were obtained, as the substance was too erratic in its behaviour to give at all satisfactory curves. Other repeated attempts by the slit method failed, principally for the reason that constancy of resistance, and hence temperature, could not be maintained. Even when the temperature apparently remained constant there was often a sudden or a gradual shift in the location of the maxima. The measurements were all made in a mercury vacuum, with the McLeod gauge showing less than 5×10^{-5} mm. of mercury.

In the measurements of e/m the centre of the molybdenite strip was maintained at a fixed potential V_0 with reference to the opposite plates by means of a connexion from a high potential battery to a point between two megohm resistances in series shunted across the strip outside the apparatus. The strip was then heated by an alternating current obtained by the commutation of a direct current. The use of an alternating current makes the effective potential entering into

equation (1) equal to the potential V_0 at the middle of the strip, no matter what the fall of potential due to the heating current or what the distribution of emission of the ions along the strip may be. This may be shown by the following argument, for which I am indebted to Professor Richardson:—Imagine the strip to be represented by a vertical line AB and the deflexion caused by the magnetic field to occur in a horizontal direction. For given values of z, H, and e/m, the magnetic deflexion x is determined at each point by the value of the potential difference V between that point and the plates. Suppose that the strip lies along the y-axis and the intensity of emission between y and $y+dy$ is denoted by $f(y)dy$. Let the actual balance position for a given value of H be x_1. Corresponding to x_1 there will, from equation (1), be a particular value V of the potential difference which will belong to a point C of the strip when the electric current is flowing in one direction, and in general, let us suppose, to some other point D when the current is flowing in the opposite direction. The condition for a balance is clearly

$$\int_A^C f(y)\,dy+\int_D^B f(y)\,dy=\int_A^D f(y)\,dy+\int_C^B f(y)\,dy$$

or

$$\int_D^C f(y)\,dy=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As $f(y)$ is necessarily positive, it follows that C and D are coincident, and as they have to have the same potential they must coincide with the only point whose potential V_0 is independent of the direction of the heating current. For this theory to hold the potentials at every point must be sufficient to saturate the emission current.

The alternating current actually used was obtained from a direct current by means of a rotating commutator with a frequency of about 20 cycles per second. This frequency was high enough for the electrometer readings to be sufficiently steady. It was not found possible to get readings actually in the break with this arrangement, as the molybdenite strip could not be induced to stay in the break. The measurements which follow were taken with very little preliminary heating,—only the amount necessary to take a series of readings of the resistance up to the start of the emission.

Remarks.	M.	Current.	*r*.	*m*/H.
Just before break.	B	D	35500	86·9
		R	„	39·5
Direct Current.		R	35000	34·4
		D	34850	43·2
		D	34700	38·9
		R	„	40·85
		R	34670	40·0
		D	„	42·6
	S	D	34400	35·95
	„	D	34200	40·55
	B	D	33720	42·45
		R	„	40·9
Commutated.	B	...	>20000	39·0
Direct current.			„	46·7
			„	48·05
Before break.			„	44·1
			„	43·65
			„	49·1
			„	40·0
			„	29·06
			„	25·02
			„	29·8
			„	54·65
			„	40·4
Break				
			3540	34·1
In second state.			2842	56·3
			3224	61·0
Dull red heat.			3230	64·6
			„	49·7
			2146	55·8
Bright red heat.			695	52·7
			728	40·1
			„	70·0
			592	78·5
			410·5	102·0
			„	59·3
Dazzling red heat.			362	75·7
			1124	94·6

(D=current in one direction; R=current reversed.)
B= balance method; S=slit method; *r*=resistance in ohms.

The curves obtained by the slit method were not at all satisfactory, and the results given above for the principal emission are only approximate. They indicate, however, that the emission was complex.

Apparently the initial emission before the break is here

almost entirely K-emission. The readings obtained with the commutated direct current are near those given by the simple direct current regardless of its direction. The steadiness of conditions with the former was by no means all that could be desired, and this was probably one of the reasons for the exceedingly wide range of values obtained at the higher temperatures. There was at one place good evidence of the appearance of Na-emission ($m/H=23$). In order to make the calculated value of m/H change from around 40 to 80, assuming that the character of the emission remains the same, it would be necessary for d to be decreased by about 2·5 mm., which is extremely unlikely, even for a temperature difference of 1000° C. Besides, such a change could be observed without difficulty from outside the apparatus. At the highest temperatures the strip was easily seen on account of its luminosity, and no bending of the strip was noticed. Since with the present arrangement ions from different parts of the strip should undergo equal deflexions, the only explanation for these results seems to be that the emission at any temperature is composed of Mo^+ ions, together with impurity emission consisting principally of K^+. The value of m/H obtained by the balance method varies with the proportion of impurities present. Inasmuch as the taking of these readings and the consequent heating were carried on continuously for a period of twenty-six hours, it is most probable that the impurity emission had been largely driven off by the end of the experiment, the permanent characteristic emission remaining.

After the experiment the distance d was measured and found to agree within ·08 of 1 per cent. with the value determined at the outset.

The curves of increase of emission with decreasing resistance (rising temperature) resembled those of an ordinary thermionic current. The decay of the thermionic current with time is quite rapid, particularly at the start. This would of course point to the presence of an impurity emission. But as the emission has seemed to be largely due to impurities in most cases, it is impossible to say whether the emission which appears to be characteristic of MoS_2 suffers a decay or not. The experiments just described, and others made with direct current heating, indicate that this emission becomes more prominent after long heating, a fact which strengthens the conclusion that it is a characteristic emission.

As a means of further investigation, the method naturally suggests itself of heating the molybdenite on a platinum

strip, as in the experiments with salts. This was tried by placing some powdered MoS_2 at the centre of a Pt strip previously glowed out at about 1100° C. The following readings were obtained :—

Remarks.	M.	R.	T.	*m*/H.
MoS_2 on strip of Pt.	B	9350	840°	72·0
		10000	755°	41·9
		„	„	41·7
		10200	786°	41·5
		10500	833°	42·35
		„	„	41·15
		„	„	41·1
		10000	755°	24·74
		„	„	41·5
New MoS_2 inserted.	B.	850	520°	39·36
		870	552°	32·04
		869	552°	38·68
		900	600°	74·4
		690	695°	48·5
		726	772°	40·35
		740	802°	40·8
		„	„	89·65
		745	811°	39·82
Fresh piece inserted.	B	750	826°	41·4
		760	845°	42·2
		770	865°	40·4
		773	873°	44·85
		783	895°	41·55
		800	930°	40·45
		750	826°	46·65
		860	1060°	40·8
		863	1070°	41·65
		872	1090°	40·25
		884	1115°	38·66
		900	1150°	46·9
		920	1191°	40·9

It is known that molybdenum combines with platinum at a high temperature, but no evidence that chemical action had taken place could be seen from the appearance of the strip after the experiment.

One notices that these values lie mainly around that for K-impurity emission. There is this departure, however : in all previous experiments when the K-emission was measured the values ranged, if anything, *lower* than the apparently

correct value, 39. Here the mean value is distinctly above this value. Furthermore, in no other case of heating a salt on a Pt strip have such high jumps in the values of m/H been experienced. Thus it may be possible that an emission of a heavy ion such as Mo^+ occurred, which most of the time was small compared to the K-emission, but which showed itself in spots where perhaps a fresh piece of MoS_2 had come into contact with the hot strip. No satisfaction could be obtained with the slit method, principally because the emission decayed so fast. Another feature of this experiment is the high temperature reached before emission was detected. This may be due simply to the small amount of the material heated as compared with the experiments with molybdenite strips.

In interpreting these results one notices the more or less constant presence of the familiar K^+-emission, which for certainly a large part of the time renders indeterminate any other emission that may occur.

The next thing to strike the attention is the occasional high value of m/H, pointing to the emission of some heavy ion, the character of which is most probably a singly-charged atom of molybdenum. The average of these high values for m/H agrees with this conclusion, as it lies in the neighbourhood of 96. It does not seem possible that an emission of Mo^{++} ions was obtained, although if such an emission occurred its presence would be next to impossible to determine.

This characteristic emission usually attains a measurable value at the start of the break, about 310° C., and may be detected anywhere beyond this point, depending upon the intensity of the accompanying impurity emission. It does not appear to be connected solely with one state or the other, or with the period of transition. More than this cannot be stated with any conviction.

9. *Summary.*

It appears from the foregoing experiments that no characteristic positive emissions are given off by the following salts:—AgCl, AgI, $PbCl_2$, $PbBr_2$, $PtCl_2$, $CuCl_2$. The same statement is probably true of AlF_3. In the case of Cu_2Cl_2 there are indications of Cu^{++}. Thus the investigation has not shed much light on the question of the connexion between valency and the charges on the ions mentioned at the beginning of the paper. In nearly every case positive ions

have been found to be present for which the value of e/m corresponds to singly charged atoms, either of potassium or sodium, or of both these elements; so that the results confirm the conclusion previously reached by Richardson *.

It is possible that the characteristic emission from these salts occurs, but is too small for measurement with the apparatus used. It will be remembered that in many of the experiments a barely noticeable emission was detected at temperatures slightly below the melting point. If the apparatus could be made more delicate, it would be interesting to see whether or not this is the case.

Molybdenite has been found to possess a number of interesting electrical properties which include the following :—

(1) In the range of temperature between that of the room and a brilliant red heat this mineral exists in two distinct states.

(2) The resistance in the low voltage or low temperature state is very nearly an inverse exponential function of the absolute temperature.

(3) At ordinary room temperatures the resistance is a function of the applied potential difference and appears to approach the value infinity as the potential approaches the value zero.

(4) The conduction of electricity is evidently carried on mainly by electrons.

Two conclusions may be stated in regard to the thermionic emission from molybdenite.

I. A large emission from impurities,—principally the ordinary K^+-emission.

II. A characteristic emission of Mo^+ ions, apparently having no exclusive relation to the break or to either state.

In conclusion, I wish to express my thanks to Prof. O. W. Richardson, who suggested the problem and under whose instruction the experiments were started, and to Prof. E. P. Adams for many helpful suggestions during the carrying on of the work. I am also indebted to Prof. Augustus Trowbridge for suggesting the test of molybdenite and for valuable advice during the trial of that substance.

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* Phil. Mag. vol. xxii. p. 669 (1911); Roy. Soc. Proc. A. vol. lxxxix. p. 507 (1914).